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ORIGINAL ARTICLE

Selective oxidation of 4-*tert*-butylphenol by hydrogen peroxide in the presence of titanosilicates

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Abstract The catalytic transformations of 4-*tert*-butylphenol in hydrogen peroxide solutions were investigated in the presence of crystalline and amorphous titanosilicates and titanium oxide. The TS-1 microporous crystalline titanosilicate was shown to exhibit low activity in the 4-*tert*-butylphenol transformation due to the steric limitations on the diffusion of the substrate molecules towards catalytic active centers. Mesoporous amorphous titanosilicates were more selective in the 4-*tert*-butylcatechol formation than the titanium oxide. The selectivity to 4-*tert*-butylcatechol in the presence of the TiO_2 did not exceed 20 mol%. The maximum 53 mol% selectivity value to 4-*tert*-butylcatechol was shown to occur over the amorphous mesoporous titanosilicate containing 1.9 wt% of Ti, the 4-*tert*-butylphenol conversion value being equal to 42 mol%.

Keywords 4-*tert*-butylphenol · 4-*tert*-butylcatechol · Hydrogen peroxide · Titanium oxide · Titanosilicate

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Introduction

4-*tert*-butylcatechol (4-TBC) was widely used as a restraining agent in the diene hydrocarbons polymerization; as a stabilizing additive for polymer materials, unsaturated aldehydes, and synthetic ethylcellulose-based resins; as an oxidation preventer for animal fat, oil, and wax [1–4].

Well-known techniques for 4-TBC synthesis were based on the alkylation of catechol by isobutylene or iso-butanol in the presence of inorganic acids, mainly sulphuric acid [3, 4]. The industrial production process was conducted in two stages: first, by the alkaline melting of o-chlorophenol or o-phenylsulphonic acid, they obtain the starting catechol, which, in its turn, was alkylated over KU-2 cationite with iso-butyl alcohol. The drawbacks of the process were the following: the formation of di- and tri- alkyl catechol derivatives, the undesired waste effluent formation, and the complex production technology.

The selective oxidation of 4-*tert*-butylphenol (4-TBP) by H_2O_2 solutions in the presence of titanosilicate catalysts could become a promising alternative for the 4-TBC production. However, there was no information in the literature regarding this matter.

Titanosilicates were widely known as an important catalysts with high activities and selectivities coupled with environmentally benign catalytic performance and play a vital role in catalytic oxidation with H_2O_2 [5]. Despite the fact that to date, two types of titanosilicate (Ti-MFI and Ti-MWW) were used in the industry, the TS-1 remained the industrial standard catalyst for oxidation reactions [5–7]. TS-1 was a crystalline microporous material of the ZSM-5 zeolite structure, where a number of silicon atoms in the lattice were substituted by the isomorphous titanium atoms. It was possible to expect that this catalyst would be low

effective for the bulky 4-TBP molecules on account of the steric restrictions. Therefore, the aim of this study was to investigate the reaction of 4-TBP oxidation by hydrogen peroxide solutions in the presence of crystalline and amorphous titanosilicates of different porous structures.

Experimental

Catalyst preparation

The TiO_2 was obtained by the hydrolysis of $TiCl_4$ in an ammonia-alcohol solution (60 mmol $TiCl_4$ and 360 mmol NH_4OH in 50 ml ethanol and 50 ml water). NH_4Cl was further removed by the stages of rinsing and thermal treatment at 550 °C for 6 h.

A sample of TS-1 crystalline titanosilicate containing 1.9 wt% of Ti was synthesized according to the technique described in [6].

The mesoporous amorphous titanosilicate catalyst samples were prepared by the sol–gel technique using the commercially available ethylsilicate-40 (ES-40) and titanium chloride alcohol solutions [8, 9]. Typically, 70 mmol of ES-40 was dissolved in 20 ml ethanol and 12 ml water. Then, the solution of $TiCl_4$ (0.87 mmol—for sample TSm-1; 1.75 mmol—for sample TSm-2; 3.50 mmol—for sample TSm-3) in 15 ml ethanol was added under stirring to produce a clear transparent gel. After gelation at 60 °C for 24–48 h, the solution of 10 mmol of ammonia in 20 ml ethanol was added. Alcogel was aged for 2 days at room temperature. The conventional drying of alcogel (12 h at 60 °C and 8 h at 120 °C) and calcination at 550 °C in air for 6 h yielded xerogel (sample TSm-1, containing 1.0 wt% Ti; sample TSm-2, containing 1.9 wt% Ti; sample TSm-3, containing 3.7 wt% Ti).

Catalyst analysis

Compositions of the synthesized titanosilicates were analyzed with the energy-dispersive X-ray fluorescent Shimadzu EDX-800HS spectrometer equipped with the rhodium anode X-ray tube operating at the voltage of 15–50 kV and the current of 20–1000 μA, the pinhole of 3–5 mm, under vacuum.

The phase composition of samples was determined with the D8 Advance Bruker X-ray diffractometer using Cuκα-emission ($\lambda = 1{,}5418$ Å, Ni-filter, 25 kV, 20 mA, $2\Theta = 10$–75, 2 min^{-1}). The qualitative and quantitative phase analysis was performed using the POWDER CELL 2.4 application program with the PCPDFWIN powder database.

The framework IR spectra of the titanosilicates were recorded in an Advance BRUKER Vertex 70 V Fourier IR spectrometer. The sample pellets were press-molded with KBr, placed into the working cell, and calcined at 350 °C followed by recording the IR absorption spectra within the range of 4000–400 cm^{-1}.

The textural characteristics were determined by the low-temperature nitrogen adsorption–desorption technique at 77 K using the Micromeritics ASAP-2020 sorption meter. Prior to the analysis, the samples were evacuated at 100–350 °C for 6 h. The specific surface square area was calculated by the BET method at the relative partial pressure of $p/p_0 = 0.2$. The pore size distribution was calculated using the desorption curve and the BJH method, and the total pore volume being determined by BJH at the relative partial pressure of $p/p_0 = 0.95$. The volume of micropores in the presence of mesopores was determined using the t-method by Halsey [10].

The distribution of the Ti atoms in the silica framework was investigated using diffuse reflectance UV–Vis spectroscopy. DR UV–Vis spectra were recorded under ambient conditions on a Shimadsu UV–VIS 2501PC spectrometer.

Oxidation procedure

The 4-TBP conversion runs were performed using the bench-scale setup with the batch isothermal reactor equipped with the stirrer (200 rpm), backflow condenser, and thermometer. A 5 ml aliquot of solvent (acetonitrile, acetone, ethanol), 0.09 g 4-TBP, and the calculated amount of the catalyst (0.1–0.6 g) were loaded into the reactor and stirred until the temperature became constant. Then, a required aliquot of the aqueous 35% H_2O_2 solution (0.06, 0.12, and 0.24 ml) was added into the reactor and the reaction start time was recorded. The feed 4-TBP concentration was 0.12 mol/l; the 4-TBP/H_2O_2 molar ratio was 1/1, 1/2, 1/4. The experiments were run at 35, 50, and 75 °C in the presence of 2.5–15 wt% of the catalyst in the mass of the feed reaction mix during 10–60 min. The grain size of the catalyst fraction used was 80–100 μm. In the preliminary experiments, the reaction mass obtained as a result of the experiment was separated from the catalyst by filtering, and the residual H_2O_2 content was determined by the iodometric titration. The high molecular weight products of the oxidative condensation were removed by filtering the reaction mix through the column loaded by the silica gel bed (the fraction of 100–200 μm).

To obtain information on the stability of active Ti species in the solid matrix, the catalyst was reused five times. The catalyst was separated by filtration after each reaction, washed with acetonitrile, and then placed into a fresh reagent mixture. On the other hand, to demonstrate that the activity of catalyst was not due to the leaching of Ti species, an additional catalytic test was performed with

filtering the reaction mix: the catalyst was fast filtered off at the reaction temperature (75 °C) and then the solution was further reacted for 60 min at 75 °C.

The products analysis was carried out by HPLC (HP 1050 with UV-detector) equipped with a C18 reverse-phase column and operated at 275 nm using 70% CH_3CN in water as a mobile phase. An internal substance, biphenyl, was used to quantify the 4-TBP and 4-TBC content.

Results and discussion

Catalyst characterization

According to the X-ray diffraction analysis, the TiO_2 was the anatase form (Fig. 1a).

The diffraction pattern of TS-1 powder was characteristic for the crystalline microporous titanosilicate TS-1 [6] (Fig. 1b).

All titanosilicate samples TSm were completely amorphous and no separate crystalline phase of TiO_2 (like anatase) was detected (Fig. 1c–e).

The IR spectrum of TS-1 and TSm samples was presented in Fig. 2. A peak assignable to the symmetric vibrational Ti–O-Si stretching can be seen at $\sim$960 cm^{-1}; while peaks at $\sim$800 and $\sim$1100 cm^{-1} can be attributed to the symmetric and asymmetric vibrational stretching Si–O–Si, characteristic of SiO_4 units with tetrahedral coordination, respectively. A typical band near 550 cm^{-1} observed for TS-1 is due to the stretching vibration SiO_4 of structural double five-membered rings in MFI-type molecular sieves framework [11]. This vibration is obviously not present in the amorphous titanosilicates.

Structural properties of synthesized samples were listed in Table 1.

It was shown from Table 1 that with increasing the Ti content in TSm samples titanosilicates, the specific surface area and the total pore volume were slightly decreased. This variation in the porous structure characteristics was attributed in [12] to the fact that when the Ti content in the titanosilicate increases, a part of it could exist as a separate oxide phase, leading to the variations in the porous structure.

Figure 3 presented the adsorption–desorption isotherms of TS-1 and TSm samples. The TS-1 sample exhibited the isotherm of type I without the hysteresis loop indicating the microporous materials. All TSm samples showed isotherm type IV with a type H3 hysteresis loop according to the IUPAC classification [10]. The formation of type IV isotherms indicated the presence of mesopores and type H3 hysteresis loop associated with the presence of aggregates of plate-like particles that advance to slit-shaped pores.

The pore size distribution (Fig. 4) derived from a BJH analysis of the desorption isotherm for mesoporous TSm samples showed a monomodal distribution centered at about 5 nm. t-Plot analysis showed that the volume of micropores was negligible (<0.02 cm^3/g). Thus, all synthesized titanosilicates of the TSm series had the mesoporous structure with a rather narrow pore distribution.

According to DRS-UV (Fig. 5), both TS-1 and TSm samples had high titanium dispersion. TS-1 showed only a well-defined band at 210 nm which is attributed to the isolated Ti atoms in a tetrahedral coordination environment. The predomination of site-isolated titanium species in the amorphous mesoporous TSm samples is indicated by absorption bands centered at 216–238 nm. The samples with high Ti content showed a slightly long-wave shift along with a band broadening, thus indicating the appearance of higher coordinated Ti atoms in oligomeric Ti species [13]. The absence of a band at 330 nm showed that anatase was not present.

Catalytic studies

The preliminary runs were conducted to demonstrate that there were no transformations of 4-TBP and H_2O_2 in the absence of a catalyst. It should also be pointed out that none of the investigated catalysts caused any transformations of 4-TBP without hydrogen peroxide. The gaseous phase composition (either air or nitrogen gas) did not affect neither the 4-TBP conversion nor the reaction product composition. Thus, under the studied conditions, both the catalyst and H_2O_2 must simultaneously present in the reactor for any oxidative transformations of 4-TBP to occur.

Catalytic properties of the synthesized titanosilicate samples were investigated in the oxidative 4-TBP transformations in the H_2O_2 acetonitrile-aqueous solutions (Fig. 6). It can be seen that the 4-TBP conversion in the presence of the TS-1 sample did not exceed 3 mol%. The low activity of the crystalline microporous titanosilicate in the 4-TBP transformation was attributed to the steric restrictions on the diffusion of 4-TBP to the catalytic active centers. In the same time, the centers remained available for the much more less in size H_2O_2 molecules. It was proven by the rather high conversion factor of the oxidizing agent occurred due to the decomposition of the latter in the pores of the TS-1 sample.

Products of the 4-TBP conversion were 4-*tert*-butylcatechol (4-TBC) and high molecular weight products of the 4-TBP oxidative condensation (tars). Under the conditions indicated in Fig. 6, the 4-TBP conversion in the presence of TSm samples amounted 57 mol%; the maximum selectivity to 4-TBC was 45 mol%. As the content of Ti increased from 1.0 to 3.7 wt% (the transition from TSm-1

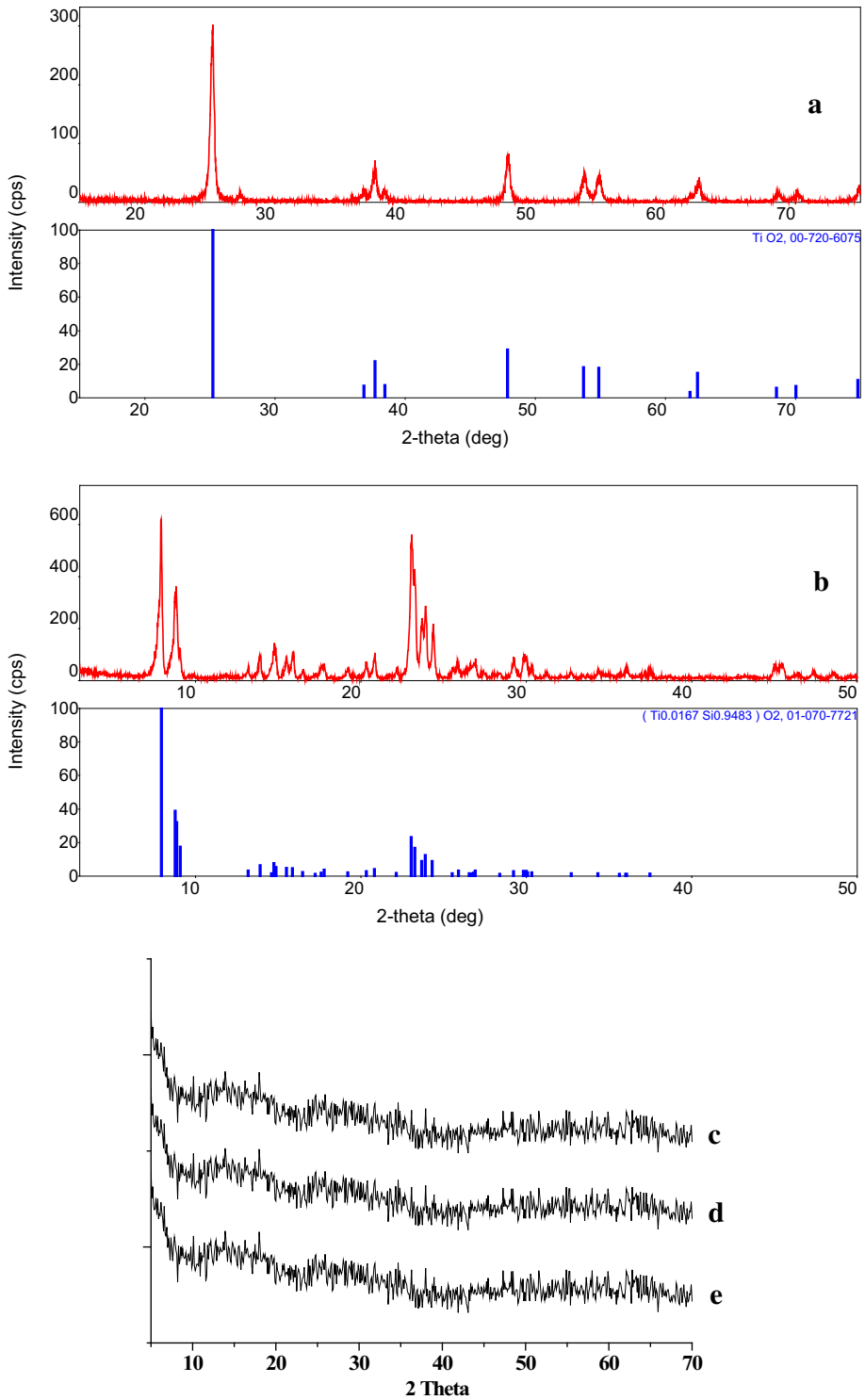

Fig. 1 X-ray diffraction pattern of TiO_2 (**a**), TS-1 (**b**), TSm-1 (**c**), TSm-2 (**d**), and TSm-3 (**e**)

sample to the TSm-3 sample), the 4-TBP conversion values slightly increased from 51 to 57 mol%, whereas the selectivity to 4-TBC decreased from 45 to 38 mol%. This fact can be explained by the appearance of partially oligomerized titanium species as the content of Ti increased (according to DRS-UV, Fig. 5). In the presence of TiO_2, the 4-TBP conversion was 30 mol% and the 4-selectivity to 4-TBC did not exceed 20 mol%.

Thus, the mesoporous amorphous titanosilicates synthesized in this work were more selective in the 4-TBC formation than the titanium oxide and a contribution of the decomposition reaction of the oxidizing agent

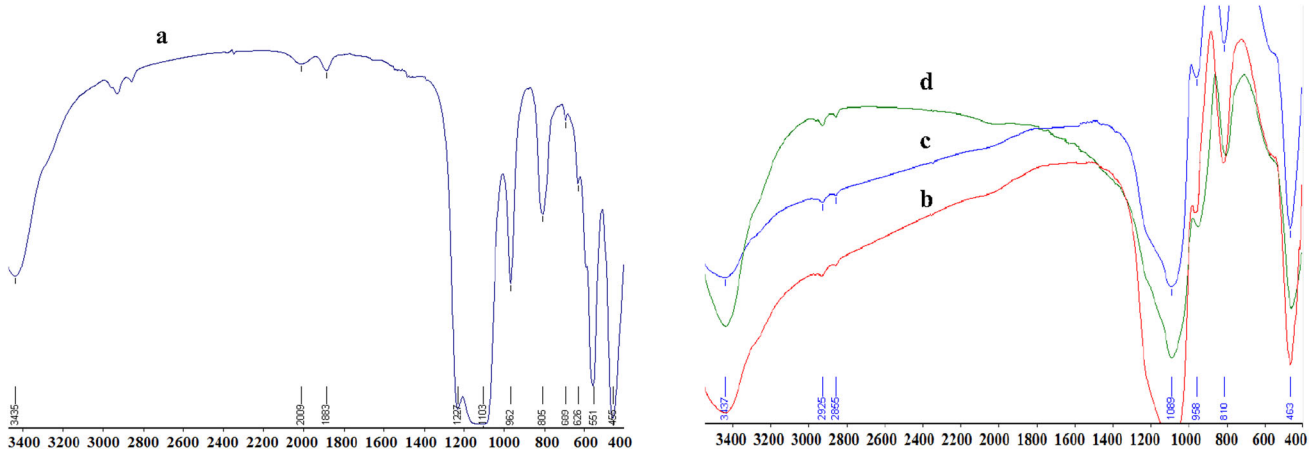

Fig. 2 IR spectra of TS-1 (**a**), TSm-1 (**b**), TSm-2 (**c**), and TSm-3 (**d**)

Table 1 Porous structure characteristics of the synthesized samples

Sample	Ti content (wt%)	Specific surface area (BET) (m^2/g)	Mesopore volume (cm^3/g)	Micropore volume (cm^3/g)
TiO_2	59.9	50	0.26	0.02
TS-1	1.9	360	–	0.21
TSm-1	1.0	560	0.99	0.04
TSm-2	1.9	505	0.92	0.05
TSm-3	3.7	495	0.89	0.05

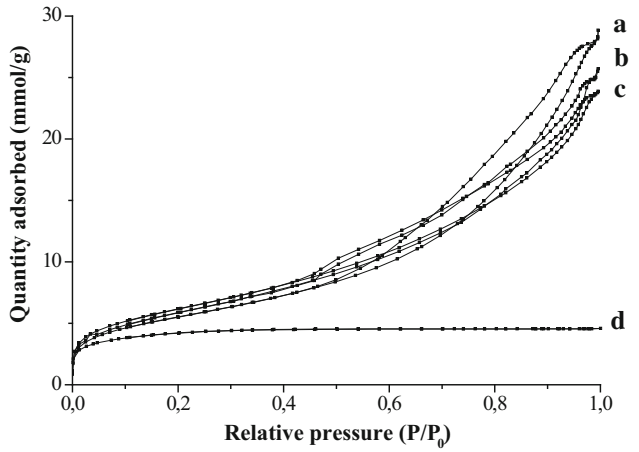

Fig. 3 Adsorption–desorption isotherms of TSm-1 (**a**), TSm-2 (**b**), TSm-3 (**c**), and TS-1 (**d**)

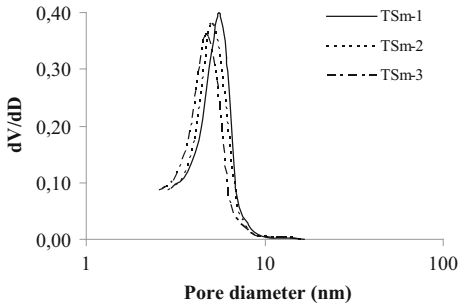

Fig. 4 Pore-size distribution for the TSm samples

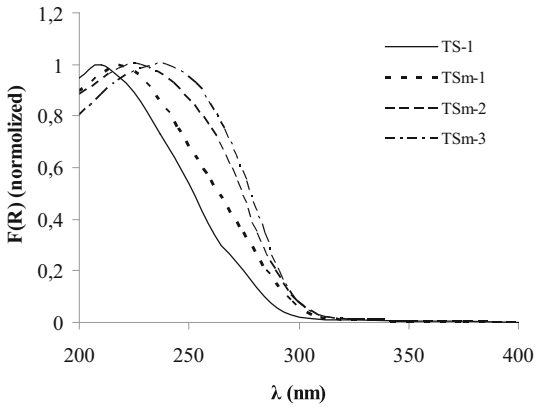

Fig. 5 DR UV–Vis spectra for TS-1 and TSm samples

molecules into water and oxygen molecules was also less.

According to the data reported in [14], the Ti atoms of the crystalline titanosilicate TS-1 existed in the tetrahedral environment of SiO-groups. By reacting with H_2O_2 molecules, they formed hydroperoxo complexes [15] selective in phenol hydroxylation. Similarly, Ti atoms in the oxide were in the octahedral oxygen environment and exhibited

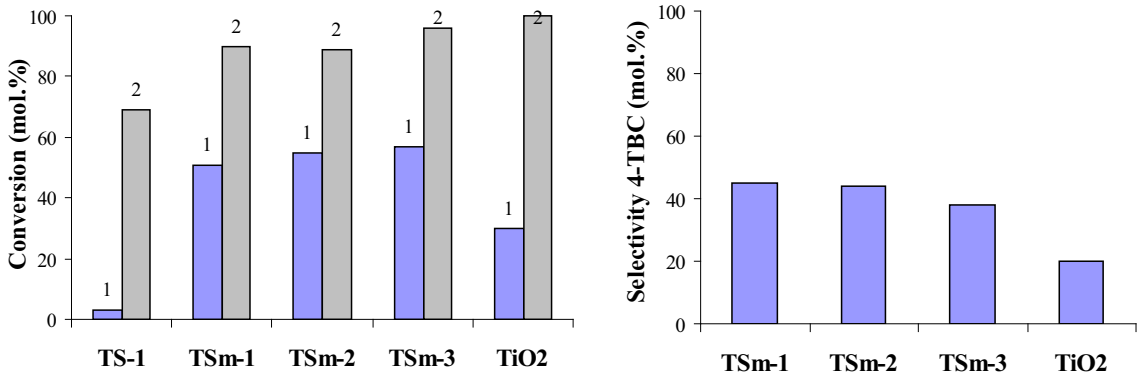

Fig. 6 Conversion of 4-TBP (*1*), H_2O_2 (*2*) and the selectivity to 4-TBC over Ti-containing catalyst (reaction conditions: 10 wt% of the catalyst; c^0(4-TBP) = 0.12 mol/l; 4-TBP/H_2O_2 = 1/2 (mol/mol); 5 ml solvent; 75 °C; 60 min) 75 °C; 60 min)

activity in the H_2O_2 decomposition. The presence of partially oligomerized titanium species catalyzed the reaction by radical chain mechanism to form products C–C and C–O coupling [16]. Our results proved this conclusion.

During the condensation stage of synthesizing amorphous titanosilicates, the incorporation of Ti atoms into the silica matrix was possible through the partial substitution of silicon atoms in the silicon-oxygen tetrahedrons. The process was accompanied by the formation of the active centers similar to those in the TS-1. Therefore, the TSm samples were more selective in the 4-TBC formation than the titanium oxide ones. Meanwhile, the titanium complexes could precipitate as the highly dispersed crystalline hydroxide phase. After the thermal treatment, it became the dioxide phase and the active in H_2O_2 decomposition and not selective in the 4-TBC formation centers were formed on the surface of it.

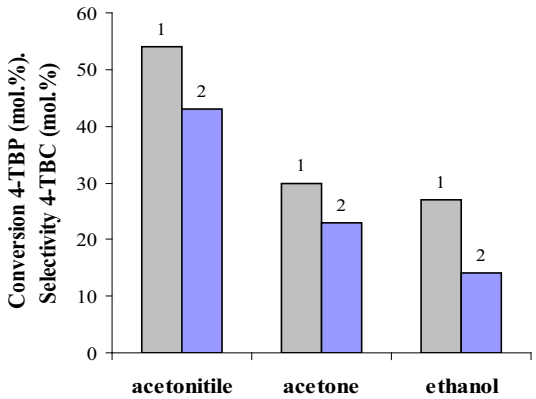

Fig. 7 Effect of solvent on the 4-TBP conversion (*1*) and on the selectivity to 4-TBC (*2*) (reaction conditions: 10 wt% of the TSm-2, c^0(4-TBP) = 0.12 mol/l, 4-TBP/H_2O_2 = 1/2 (mol/mol), 5 ml solvent, 75 °C, 60 min)

Effect of reaction parameters

The application of a polar solvent is known [14] as the favorable factor to decrease the homolytic H_2O_2 decomposition that yields various radical oxo-intermediates and leads to the non-selective oxidation. Besides, similar to the phenol hydroxylation with H_2O_2 [17], we may assume that the reaction of the selective 4-TBP oxidation to 4-TBC with H_2O_2 over amorphous mesoporous titanosilicate also occurs via heterolytic oxygen atom transfer mechanism (electrophilic hydroxylation) [16]. And there is a number of recommended solvents for the latter, namely, water, methanol, ethanol, acetic acid, acetone, acetonitrile, DMSO, DMPA, nitromethane, and sulpholane [18]. In Fig. 7, the results of the 4-TBP oxidation by aqueous H_2O_2 solution in the presence of TSm-2 sample are given for different solvents, namely, acetonitrile, acetone, and ethanol. In acetone and ethanol solvents, the 4-TBP conversion values are close, the selectivity to 4-TBC being higher in acetone than in ethanol. The highest 4-TBP conversion of 54 mol% and the highest selectivity to 4-TBC of 43 mol% are observed in the acetonitrile medium.

Results of the studies presented in Table 2 illustrated the influence of the catalyst amount, temperature, and 4-TBP/H_2O_2 molar ratio on the 4-TBP and H_2O_2 conversions and on the selectivity to 4-TBC in the presence of TSm-2 sample. It can be seen that the 4-TBP and H_2O_2 conversion values were minimum in the presence of 2.5 wt% of titanosilicate at 35 °C, being 11 and 23 mol%, respectively. The increase in temperature up to 75 °C caused more than 3-fold increase in the 4-TBP and H_2O_2 conversion up to 38 and 76 mol%, respectively. As well, the increase in temperature from 35 °C up to 75 °C led to the increase in the selectivity to 4-TBC. The maximum selectivity to 4-TBC in the presence of 2.5 wt% amount of the catalyst at 75 °C was 42 mol% at the 4-TBP conversion of 38 mol%.

In the presence of 10 wt% of the catalyst, the increase in temperature from 35 up to 75 °C led to the higher 4-TBP conversion from 25 to 54 mol%. The selectivity to 4-TBC

Table 2 Influence of the TSm-2 catalyst amount, temperature, and 4-TBP/H_2O_2 molar ratio on the conversion of 4-TBP, H_2O_2, and the selectivity to 4-TBC

Catalyst amount (wt%)	T (°C)	4-TBP/H_2O_2 (mol/mol)	Conversion H_2O_2 (%)	Conversion 4-TBP (mol%)	Selectivity 4-TBC (mol wt%)
2.5	35	1/2	23	11	35
	50	1/2	35	16	36
	75	1/2	76	38	42
10	35	1/2	41	25	47
	50	1/2	79	38	52
	75	1/1	100	30	45
		1/2	89	54	43
		1/4	53	62	30
15	35	1/2	58	32	48
	50	1/2	92	42	53
	75	1/2	100	38	40

Reaction conditions: c^0(4-TBP) = 0.12 mol/l, 5 ml CH_3CN, 60 min

Table 3 Stability test of TSm-2 catalyst

Catalytic cycle	Conversion H_2O_2 (%)	Conversion 4-TBP (mol%)	Selectivity 4-TBC (mol%)
1	89	54	43
2	86	53	43
3	86	53	44
4	84	54	44
5	85	53	43

Reaction conditions: 10 wt% of TSm-2, c^0(4-TBP) = 0.12 mol/l, 4-TBP/H_2O_2 = 1/2 (mol/mol), 5 ml CH_3CN, 75 °C, 60 min

values was higher at the same 4-TBP conversion value, namely, the maximum the selectivity to 4-TBC was 52 mol% at the 4-TBP conversion of 38 mol% at 50 °C.

An increase in the catalyst content from 10 up to 15 wt% at 35 and 50 °C allowed to maintain rather high 4-TBC formation selectivity values as well as the higher selectivity to 4-TBC.

An increase in the oxidizing agent quantity (the higher 4-TBP/H_2O_2 molar ratio from 1/1 to 1/4) results in the slightly higher 4-TBP conversion from 30 to 62 mol%; however, the selectivity to 4-TBC markedly decreases from 45 to 30 mol%.

It should be noted that no changes in 4-TBP conversion and the selectivity to 4-TBC were observed during the five catalytic cycles (Table 3), indicating that the catalyst was stable under reaction conditions. Moreover, no further 4-TBP conversion was exhibited in filtrate after removal of the catalyst. Thus, it was proved that the 4-TBP oxidation with H_2O_2 is a true heterogeneous process, during which no titanium leaching from the silicate matrix occurs [19].

The dependence of 4-TBP, 4-TBC, and tars content on reaction time was displayed in Fig. 8. The tars content

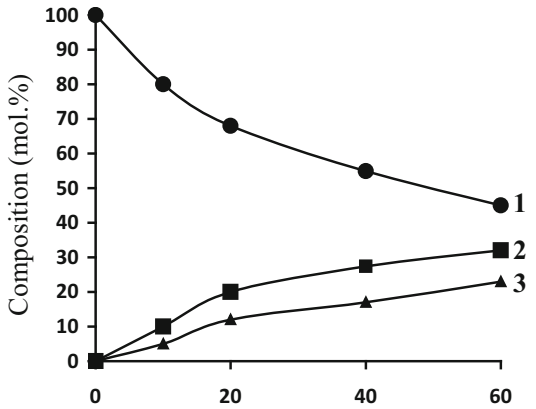

Fig. 8 Influence of the reaction time on the 4-TBP (1), 4-TBC (2), and tars (3) content (reaction conditions: 10 wt% of the TSm-2, c^0(4-TBP) = 0.12 mol/l, 4-TBP/H_2O_2 = 1/2 (mol/mol), 5 ml solvent, 75 °C, 60 min)

changing indicated that the oxidative condensation products were formed at the initial time. It should be noted that 4-TBC also converted to oxidative condensation products with up to 80% conversion under the reaction conditions (10 wt% of TSm-2, 75 °C, 4-TBC/H_2O_2 = 1/2, 60 min).

The following reaction scheme was proposed on the basis of these data (Fig. 9).

Conclusion

The influence of chemical and phase composition of the titanium-containing porous materials on their catalytic activity in the 4-*tert*-butylphenol oxidation with hydrogen peroxide in acetonitrile-aqueous solutions was investigated.

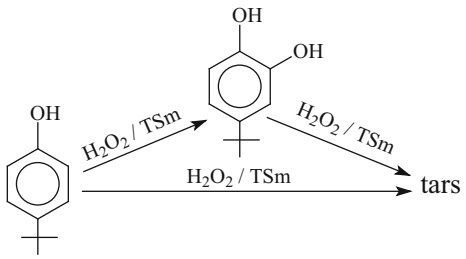

Fig. 9 Scheme of the 4-TBP oxidative transformations in the H_2O_2 acetonitrile-aqueous solutions over titanosilicate catalyst

The TS-1 microporous crystalline titanosilicate exhibited low activity in the 4-*tert*-butylphenol transformation in acetonitrile-aqueous H_2O_2 solutions due to the steric restrictions on the diffusion of the substrate molecules into the channels of the catalyst.

Mesoporous amorphous titanosilicates with the Ti content within the range of 1.0–3.7 wt% showed good activity in the 4-*tert*-butylphenol conversion and the selectivity to 4-*tert*-butylcatechol. The maximum 53 mol% selectivity to 4-*tert*-butylcatechol (4-*tert*-butylphenol conversion—42 mol%) was reached at the temperature of 50 °C for 60 min reaction time in the presence of 15 wt% of the mesoporous titanosilicate containing 1.9 wt% of Ti.

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